DEVELOPMENT OF BAYER GEOPOLYMER PASTE AND USE AS CONCRETE

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Abstract

The Centre for Sustainable Resource Processing (CSRP) (www.csrp.com.au/) had a vision of sustainable minerals processing, where global material needs are satisfied with significantly reduced impacts. One legacy of that vision has been the establishment of the Geopolymer Alliance (www.geopolymers.com.au/) and the continued development of geopolymers utilising industry co-products. Of particular interest here is the utilisation of bauxite refining co-products within geopolymer production.

Collaborative research between Alcoa of Australia Limited and Curtin University of Technology (Curtin) set out to investigate the use of Bayer process materials for the production of geopolymers. Secondly, if incorporation was possible, could the resulting paste be utilised as binder for concrete formulations.

Research was conducted over several years with the following outcomes.

- Sodium silicate activation solution could be replaced by a Bayer sodium aluminate solution without detrimental impact upon compressive strength.
- "Bayer Geopolymer" paste was refined from an oven cured product to ambient cure, with compressive strength in excess of 30 MPa.
- The ambient setting paste was applied to a concrete mix design, with resultant compressive strength in excess of 25 MPa.

Clearly there is opportunity for significant synergy between the Bayer Industry and the Geopolymer Industry, with both having the potential to benefit. There is now also potential for other Bayer products (Mud, Sand, Lime etc.) to be included within the concrete mix design.

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1. Introduction

Alcoa of Australia Limited (Alcoa) has long recognised bauxite residue as an unutilised resource. Following several decades investigating opportunities to produce economically viable products from bauxite residue, three high volume products were identified; Red Sand™, Alkaloam® and Red Lime™ (Jamieson et al, 2005). These products were refined and assessed as part of the Centre for Sustainable Resource Processing (CSRP). One product (Red Sand™) was progressed to a point of utilisation within road construction (Jamieson et al 2008).

While these high volume products may make a significant impact upon residue volumes, it is the ability to utilise multiple products in various applications that will ultimately lead to utilisation of the vast untapped resource. One application that was explored was the utilisation of residues within geopolymer formation (Hart et al, 2006; Avraamides et al, 2010).

1.1 What is a Geopolymer?

Geopolymers are inorganic aluminosilicate polymers (ie mineral polymers), where the backbone structures are chains made up from aluminate and silicate. They can also be described as alkali activated alumino silicates. Geopolymers require a high caustic concentration to allow the dissolution, reaction and precipitation via a condensation process. Barbosa et al (2000) and Davidovits (2005) have published representations of the backbone chains and linkages.

These mineral polymer structures harden with significant cross linking to form a material with high compressive strength. This has led to geopolymers being considered as a binder for the formation of concrete and many potential industrial applications including; concrete pathways & retaining walls Zeobond Pty Ltd (2011), railway sleepers, wall panels and acid resistant sewer pipes (Gourley & Johnson 2005). Geopolymers have also been investigated for stabilisation of waste and even for internment of intermediate level nuclear wastes as reviewed by Vance and Perera (2009).

Geopolymers have great potential as a disruptive or transformational innovation because of their wide variety of distinctly superior properties compared to Ordinary Portland Cement (OPC). These include a significantly lower green house gas footprint, superior compressive strengths, acid resistance (especially sulphuric), superior high temperature performance, fire resistance and smaller shrinkage and creep (McClellan et al, 2011, Rangan et al, 2008; Rickard et al, 2010). In addition, geopolymers can be made from high volume, under utilised by-products such as flyash, steel making slag and waste alkali. A review of technology was published by Davidovits 2008, Provis and van Deventer (2009).

The acceptance of geopolymer concrete into the conservative construction industry has been slow but is gaining momentum. RILEM (The International Union of Testing and Research Laboratories for Materials and Structures) are about to release a state of the art report. The Victorian Government has included geopolymers in their paving specifications and the Concrete Institute of Australia has released an application note on geopolymers. There are several companies in Australia now offering geopolymer concrete options.

1.2 What is Alcoa Technology Delivery Group's (TDG) Involvement?

TDG's initial interest in geopolymers revolved around the incorporation of alkaline residues. The residues primarily acted as filler with the small alkaline content providing some offset against the caustic demand for product formation. Ultimately the process held minimal synergy and was limited to fresh residue with minimal carbonation of residual caustic. In addition there was a significant loss of geopolymer strength with the high required rates of residue use.

As with other by-product developments, the thinking was reversed. Rather than accept the "end of pipe" paradigm, the question was asked "how could we engineer a product that would be competitive as an activation reagent for geopolymer production?" The answer was the realisation that industrial grade by-products could be made to purpose and result in significant alumina industry benefit. Therein, the supply of Bayer solution would actually result in an impurity bleed to the process, when it is replaced with raw caustic and additional bauxite (Jamieson 2006 WO/2008/017109).This counter intuitive discovery has led to the significant geopolymer product development that is described below.

2. The Activator

The formation of geopolymers requires the use of caustic activator solutions to initiate dissolution of the raw alumino-silicates. These can be either silicate or aluminate solutions. In this case, the raw alumino-silicates were blends of local West Australian fly ash from either Muja or Collie power stations and silica fume from Australian Fused Material (Kwinana).

The first task of research was to progressively phase out the fresh caustic silicate solution and replace it with Bayer liquor for a paste formulation. In these initial laboratory experiments, geopolymers were oven cured at 70°C in sealed plastic vials. Samples were analysed for compressive strength in triplicate and the average shown in Figure 1.

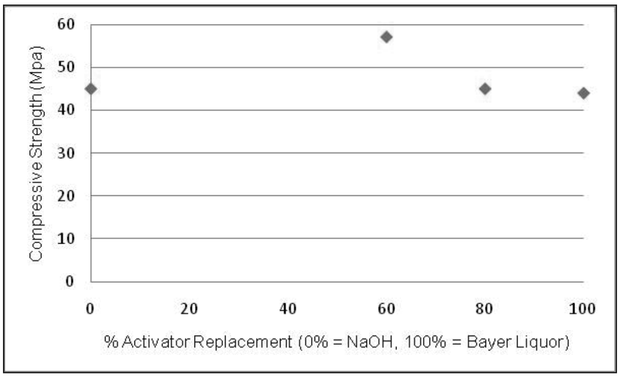

Figure 1. Day 7 compressive strength of paste samples showing progressive replacement of caustic with Bayer liquor.

As can be seen, the results for paste show minimal impact upon strength as increasing amounts of Bayer liquor are used to replace the sodium hydroxide activator. Strengths are maintained above 40 MPa, for comparison, footpath concrete is typically 10 – 15 MPa, house pad concrete is about 24 MPa, and sea wall armour is in excess of 50 MPa.

3. The Paste

Bayer activated geopolymer paste samples have shown significant strength in excess of 40 MPa, retain their efficacy when immersed in water, and can be formulated to prevent efflorescence. In addition, there is a predictable shift in the amorphous hump for the geopolymer compared with silica fume and fly ash (Williams et al. 2011).

SEM evaluations of the fracture faces of freshly broken samples in Figure 2 clearly show partially and un-reacted fly ash spheres encased in a non-crystalline matrix. There is no observational change to the formation of amorphous binding agent as the silicate activator is replaced with Bayer activator solution.

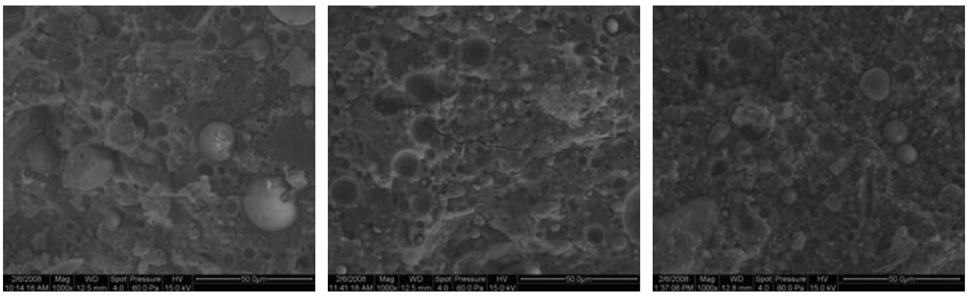

Figure 2 SEM of Bayer activated material (ambient cure).

4. The Ambient Cure

The majority of flyash and metakaolin based geopolymers are cured at elevated temperature, typically 70 – 90°C, for rapid strength gain. Hardjito & Rangan (2005) have demonstrated optimised strength gain for steam cured geopolymer concretes. However, the majority of conventional concrete is currently cured at ambient temperature. Therefore it is critical that geopolymers are designed to have similar usage patterns to ordinary Portland cement.

Curing of geopolymers at ambient temperatures can be achieved through the addition of small amounts of calcium to the mix. Calcium can be added through direct addition of lime, or through addition of other calcium rich alumino-silicates such as blast furnace slag. A series of tests indicated that 2.5% Ca was sufficient to ensure ambient curing while achieving suitable compressive strength at 7 days (Figures 3 & 4). Compressive strength was observed to continue to improve with time.

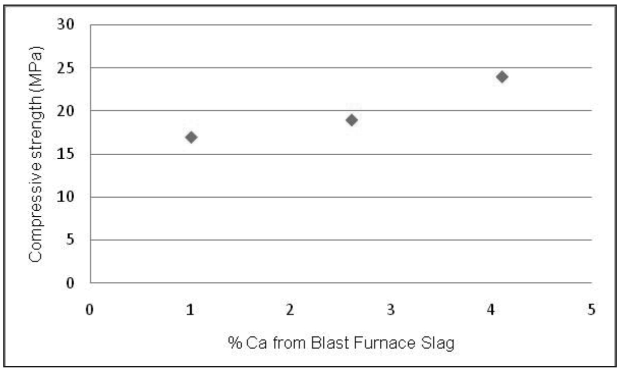

Figure 3. Day 7 compressive strength of geopolymer paste with addition of blast furnace slag, cured at ambient, with good workability.

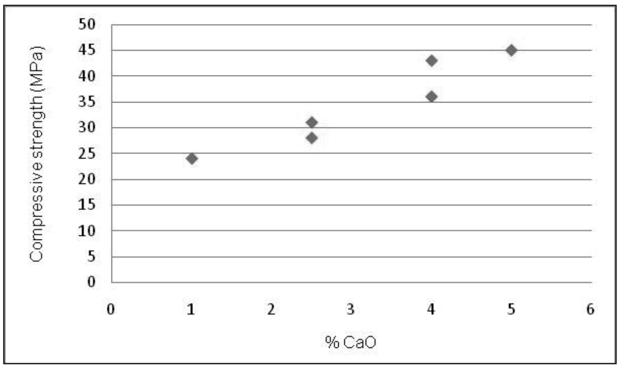

Figure 4. Day 7 compressive strength of geopolymer paste with addition of calcium oxide, cured at ambient, with good workability.

5. Development of Bayer geopolymer concrete

Addition of sand and aggregate to the geopolymer paste resulted in geopolymer concrete with typical compressive strength of 25-30 MPa. As more aggregate is added workability is reduced but with super plasticisers, as used with OPC concrete, this can be rectified. Figure 5 shows the cross section of a Bayer liquor geopolymer concrete while Figure 6 shows a paver.

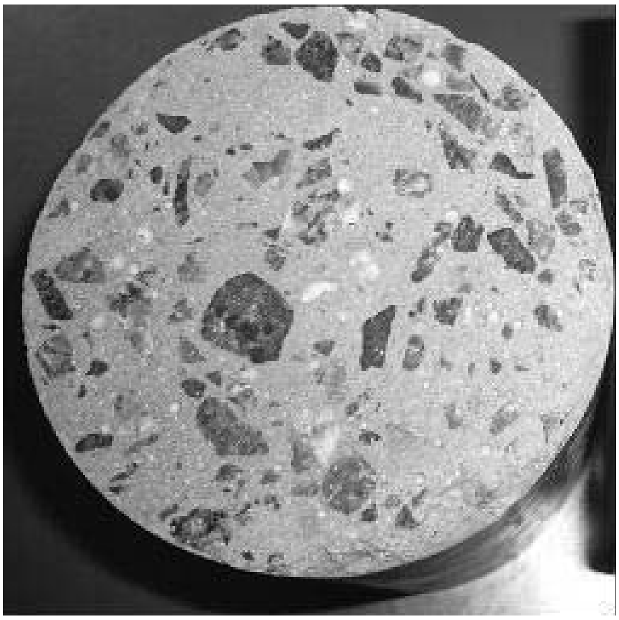

Figure 5. Close up on aggregate in Bayer Geopolymer.

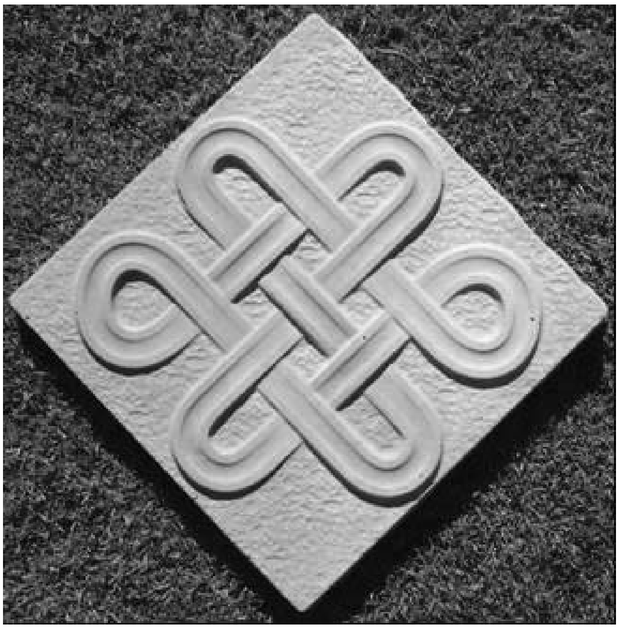

Figure 6. Decorative paver made from Bayer Geopolymer.

However there are some potential difficulties for the widespread adoption and use of geopolymers and Bayer derived geopolymers.

Generally geopolymer concrete is stiffer and less workable than OPC based concrete with similar compressive strength. This is not an issue for preformed products but could be a problem for high volume high slump applications. Training and possible certification would be required for concrete crews. Admixtures more suited to geopolymer chemistry also need to be developed to control workability.

Geopolymers can also have a degree of adhesion dependant upon the starting materials and composition. This can be advantageous for spray coating applications, for mine backfill or slope control applications but would prove difficult if a smoothed finish is required. This is mainly controlled through composition selection, but would also be improved with development of admixtures more suited to geopolymer chemistry.

6. Geopolymer and alumina industry synergy

The alumina industry has significant overlap in technology with the needs of geopolymers.

A few of the opportunities are listed below.

- The alumina industry has traditionally underpinned the demand and supply of caustic.
- The alumina industry is established with significant teams of skilled scientists, engineers and operators knowledgeable in the handling and use of aluminate solutions.
- The alumina industry already has established QC/QA capability on aluminate solutions.
- The alumina industry has significant quantities of "low value" steam (ie atmospheric pressure and <100C), suitable for steam cure of geopolymer concrete.
- The alumina industry is established with significant infrastructure such as road, rail and port hubs.
- Secondary commodity products from the alumina industry are potentially synergistic with geopolymers (e.g. sand, lime).
- The alumina industry is a robust industry consuming significant quantities of concrete.

7. Conclusions

It has been demonstrated that Bayer process liquors can be produced to a standard suitable for use in production of geopolymer binder. This binder has then been demonstrated to make concretes which are typically superior on several measures to OPC concrete (eg tensile strength, acid resistance, CO_2 footprint). Increasing knowledge of the advantages of geopolymer concrete over cement based concrete, should promote further development towards market acceptance.

There is a large opportunity for significant synergies between the alumina and construction industries, be it in use of sand, lime, clay, geopolymer or energy. With the community expectation that all industry will move towards greater sustainability, such synergies should be explored to maximise community benefit from the resources industries. It will be a key pillar in our future public license to operate.

8. Acknowledgements

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